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(54) **Compositions and solventless process for digital laser imageable lithographic printing plate production**

Zusammensetzungen und lösungsmittelfreies Verfahren für die Herstellung von Flachdruckplatten, auf welche mittels Laser digital aufgezeichnet wird

Compositions et procédé sans emploi de solvants pour la fabrication de plaques lithographiques pour l' enregistrement digitalisé par laser

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Description

[0001] This invention relates to novel, long impression life, digitized laser imageable lithographic printing plates and to the method for their production. The invention especially relates to lithographic printing plates for dry or waterless lithographic printing operations. The invention particularly relates to the production of waterless, laser ablatable lithographic printing plates employing a solventless coating process that substantially reduces the amount of volatile organic components (VOC) released during the process.

[0002] In conventional planographic printing, a printing plate bearing an oleophilic, ink receptive image is first dampened with an aqueous fountain solution to prevent ink from wetting the hydrophilic, non-image bearing areas of the printing plate, after which an oil-based ink is rolled over the plate to selectively coat the now printable image. Conventional planographic printing has some difficulties inherent in having both an oleophilic ink and an aqueous fountain solution conjoined in the same press. Problems include the fountain solution flowing back into the train of inking rollers on the press; control of the delicate balance needed between the amount of ink and the amount of fountain solution applied to the printing plate; fountain solution flowing forward over the offset cylinder, moistening the copy paper and thereby causing its dimensional change; and in the case where printing is imaged directly by electrophotography, the imaged printing plate must be subjected to an etching treatment and the printing operation becomes complicated.

[0003] Considerable effort has been applied in the industry directed toward the development of lithographic printing plates that may overcome some of the foregoing problems.

[0004] US-A-4,259,905 teaches a waterless, contact speed planographic printing plate having an overlaying modified organopolysiloxane polymeric material layer. The plate exhibits enhanced printing endurance and produces prints of low background contamination.

[0005] US-A-4,342,820 teaches a negative working waterless plate requiring no dampening water for use in negative work which comprises a base substrate, a light releasing photosensitive layer overlaying the base substrate and the silicone rubber layer overlaying the photosensitive layer. When the printing master plate is exposed through a negative film and then treated with a developer, only the silicone rubber layer overlaying the exposed photosensitive layer is removed, while the photosensitive layer remains as it is to form an image area. Dampening water is not required when printing is carried out.

[0006] US-A-3,894,873 teaches a positive working waterless plate comprising a substrate, a light sensitive photoadhesive layer overlaying the substrate and a silicone rubber layer overlaying the photoadhesive layer. When the printing master plate is exposed through a positive transparency and then treated with a developer, only the silicone rubber layer overlaying the unexposed photoadhesive layer is removed, while the photoadhesive layer remains as it is forms an image area.

[0007] The foregoing waterless lithographic plates are prepared by conventional photographic image transfer. While relatively efficient and efficacious, it is a multi-step, indirect process of constrained flexibility. However, artisans in the field of lithographic plate production have recently come to bend their efforts toward the development of a means to integrate digitally controlled image-making technology, i.e., the ubiquitous PC computer of todays world, with a means to directly convey the digital image onto a lithographic plate that will be usable for large production runs (100,000 or more copies).

[0008] Lasers and their amenability to digital control have stimulated a substantial effort in the development of laser-based imaging systems. Early examples utilized lasers to etch away material from a plate blank to form an intaglio or letterpress pattern. See., e.g., US-A-3,506,779 and US-A-4,347,785. This approach was later extended to production of lithographic plates, e.g., by removal of a hydrophilic surface to reveal an oleophilic underlayer. See, e.g., US-A-4,054,094. These systems generally require high-power lasers which are expensive and slow.

[0009] US-A-5,339,737, US-A-5,353,705 and US-A-5,351,617 also describe lithographic printing plates suitable for digitally controlled imaging by means of laser devices. Here, laser output ablates one or more plate layers, resulting in an imagewise pattern of features on the plate. Laser output passes through at least one discreet layer and imagewise ablates one or more underlying layer. The image features produced exhibit an affinity for ink or an ink-abhesive fluid that differs from that of unexposed areas. The ablatable material used in these patents to describe the image is deposited as an intractable, infusible, IR absorptive carbon black or conductive polymer under an IR transparent polymer film. As a consequence, the process of preparing the plate is complicated and the image produced by the ablated polymer on the plate does not yield sharp and distinct printed copy.

[0010] Crosscutting all of the old and new technologies for production of lithographic plates, be they conventional or waterless, digitized image formation or phototransfer, are the environmental concerns regarding the emission into the atmosphere of the organic chemicals used as solvents in lithoplate coating operations. A new imperative has been placed upon the printing industry to reduce exposure to organic solvents in the work place as much as possible. This has devolved into an imperative upon the artisan to reformulate plate production to reduce VOC from the lithographic plate production process as much as possible. So as the industry moves to develop ever better waterless plates or ever better digitized-imageable plates it is important to do so within the context of an ever more environmentally friendly

lithographic plate production process.

[0011] Accordingly, one objective of the present invention is the development of lithographic plate compositions that are imageable by digital image-inscribing processes.

[0012] Another object of the present invention is the development of digital imaging lith plate compositions that can be employed in waterless printing processes.

[0013] Yet another object of the invention is the development of processes to produce the foregoing digitizable, waterless lithographic plates in a solventless system at low VOC.

[0014] The objectives of the invention have been realized through a series of discoveries relating to the use of solventless polymeric species and/or precursors selected to contain residual crosslinking functionality. The species are converted to an IR laser ablatable polymeric intermediate layer between a substrate and a top coating. The residual crosslinking functionality serves to bond with an oleophobic and hydrophobic top coating used to provide a waterless printing capability that also contains residual crosslinkable functionality. The ablatable layer can also bond with a prime insulating coating which may be deposited on a metallic substrate, if preferred. The resulting coatings on the plate, bound to each other by a crosslinked structure, exhibit extraordinary adhesive strength and, thus, high printing impression life. Because the coatings or layers are formed using neat or solventless liquid monomers, oligomers or polymers, VOC emissions are reduced.

[0015] The lithographic plates prepared according to the invention exhibit a combination of properties unique compared to lithographic plates in the art heretofore:

- digitally controlled image formation;
- waterless lithographic printing;
- low organic chemical emissions during plate production;
- long printing life, i.e, greater than 100,000 copies.

[0016] More particularly, the invention comprises a waterless, multilayered lithographic printing plate imageable by laser ablation exhibiting superior impression life and low volatile organic components containing a first solid substrate layer; a second infra-red light absorbing polymeric layer containing crosslinking functionality; a polysiloxane top layer containing crosslinking functionality, wherein said second layer and top layer contain interlayer crosslinking bonds. Optionally, the plate may contain a prime polymeric layer interposed between the first and second layer. The prime layer also contains crosslinking functionality connected to the second layer plus pigments or dyes to distinguish image bearing and non-image bearing areas of the image-ablated plate.

[0017] The invention more particularly comprises a layered image recording surface or material produced by a solventless process and imageable by IR laser ablation to provide a desired image. The image recording surface comprises a first infra-red light absorbing polymeric layer containing crosslinked functionality. A second layer comprises a polysiloxane layer containing crosslinked functionality, wherein said first layer and second layer contain interlayer crosslinked bonds.

[0018] The process for preparing the plate of the invention comprises coating a solid substrate with a solventless mixture of polymerization initiators and polymerizable, liquid monomers, oligomers or polymers having crosslinking functionality. The plate is then exposed to UV light to partially polymerize the coating and form an IR absorbing coating. The partially polymerized coating is coated with a polysiloxane containing crosslinking functionality and the polysiloxane is exposed to UV light to partially polymerize that coating. Finally, the plate is thermally treated at elevated temperature for a time sufficient to complete the polymerization and crosslinking reactions.

Composition of the Waterless Lithographic Plate

[0019] The lithographic printing plate precursor of the invention is constructed of a substrate with two or three layers deposited on the substrate.

The Substrate Layer

[0020] The substrates which can be used in the instant invention are those having the mechanical strength needed to withstand the rigors of the printing process in which it is used. Solid substrates can be manufactured from metal, wood, film, or composite material. Since the printing process in which the plate is used is a waterless process, the substrate is not restricted to those having a hydrophilic surface as conventionally practiced. The substrate useful in the invention can have either a hydrophilic or hydrophobic surface. An aluminum substrate is preferred in view of its mechanical strength and the familiarity of that substrate to the printing industry.

The Second Layer

[0021] The second layer is a crosslinked polymeric coating that contains unreacted or residual crosslinking functionality as formed. Preferably, the second coating is initially formed as a partially polymerized coating and polymerization is completed after a top coating is applied to it. An important attribute of the second layer is strong absorption in the infra-red portion of the electromagnetic spectrum - an attribute key to the intended IR ablative role of the layer. Strong IR absorption can be achieved by an appropriate selection of the chemical structure of the polymeric coating, by the addition of pigments or other IR absorbtive chemicals, or both. Preferably, the coating contains carbon black.

[0022] The second coating is formed by the polymerization of monomers, oligomers or polymers, or mixture thereof, employing free radical, cationic, anionic or thermal polymerization initiation. Preferably, liquid monomers, oligomers or polymers are coated on the substrate to avoid the use of volatile organic solvents. The use of liquid monomers, oligomers or polymers provides a process that is solventless, i.e., free of volatile organic components below a boiling point of 150°C. Consequently, the plate production work-place is not adversely affected by the emission of organic solvents. As applied, the coating contains polymerization initiators plus pigments, dyes and surfactants as necessary.

[0023] A particularly useful class of initiators are those photoinitiators which release free radicals or cations when exposed to UV light. Once the second coating has been deposited polymerization is initiated and partially completed by using UV light to release the specific polymerization initiator. Non-limiting examples of photoinitiators that can be used in the invention include Sartomer CD1010 (Sartomer) for polymer precursor systems that polymerize by cationic polymerization and Irgacure 369 (Ciba) and Quantacure ITX (Octel Chemicals) for polymer precursor systems that polymerize by free radical polymerization.

[0024] Free radical photoinitiators useful in the instant invention are listed in the text of "Chemistry and Technology of U.V. and E.B. Formulations for Coatings, Inks and Paints", P.K.T. Oldring - Editor, SITA Technology LTD., Gardiner House, pp 276-298.

[0025] These photoinitiators include benzoin and benzoin ethers, benzilketals, dialkoxyacetophenone derivatives, hydroxyalkylphenones, aminoalkylphenone derivatives, benzophenone derivatives and 1,2-diketones, among others.

[0026] Photoinitiators for cationic polymerization as carried out in the instant invention include: aryldiazonium salts, diaryliodonium salts, triarylsulfonium salts, triarylselenonium salts, dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts and ferrocenium salts.

[0027] The polymer systems and precursors that can be used to form the second layer are limited only to those systems that can undergo polymerization in situ on the plate to yield a polymer or partially polymerized polymer that contains residual crosslinkable functional groups. These functional groups are intended to form crosslinking bonds with similarly available functional groups in the top coating or, in addition, a prime coating. Preferably, the polymer precursors are applied neat in a liquid state in a mixture that avoids the use of organic solvents. Useful monomers, oligomers or polymers containing crosslinkable functional groups include epoxide, hydroxy, carboxy, isocyanate, acrylate, vinyl, amino, silane, halohydrin, sulfonate, formyl and aliphatic and aromatic acid anhydrides. Especially useful polymers are polyethers containing residual epoxy groups.

The Top Layer

[0028] The top layer consists of a silicone rubber such as a cross-linked diorganopolysiloxane, transparent to infrared light. A preferred polysiloxane is a divinyl terminated polysiloxane. Polysiloxanes containing glycidyl groups, pendant hydroxy groups or hydro-methyl siloxane can also be used. As applied to the second coating, the polysiloxane includes photoinitiators and crosslinking agents. When exposed to UV light the coating is crosslinked. Subsequent heating completes the polymerization with formation of crosslink bonds between the residual groups of the second and top layers.

The Prime Layer

[0029] Optionally, a prime coating may be deposited first on the substrate plate which is similar to the composition of the second layer except that it does not contain carbon black. Rather, the prime coating contains pigments or dyes which help to distinguish the image formed on the plate by IR laser inscription. The prime coating also serves to provide insulation between the second layer and the aluminum substrate so that heat losses to the substrate are diminished during IR imagewise ablation of the second layer.

[0030] The following Example 1 illustrates the preparation and application of the lithographic plate of the invention. The example illustrates the invention using an optional prime coat on the substrate. Polymerization of the coating is initiated cationically by employing photoinitiators which convert to cationic polymerization initiators upon exposure to UV light.

EXAMPLE 1

[0031] The composition of the prime coat follows:

Ingredients	Suppliers	Weight(%)
Limonene Dioxide	Atochem	20 -40
1,3-Butadiene homopolymer internally epoxidized	Atochem	20 - 40
Cyracure UVR 6110	Union Carbide	20 - 40
Pigment	Sun Chemical	0 - 20
Sartomer CD 1010	Sartomer	2 - 10
Byk-361	Bykchemie	0 - 2

[0032] Cyracure UVR 6110 is a 3,4-epoxy cyclohexyl methyl-3',4'-epoxy cyclohexyl carboxylate. Sartomer CD1O1O is triarylsulfonium hexafluoroantimonate in propylene carbonate which was used as initiator. Byk-361 is an acrylic polymer which was used as a wetting agent. Pigments or dyes having different color were also used in the formulation to enhance the color contrast between the image and non-image areas. The solution was coated on the smooth aluminum substrate using a wire-wound rod to give a uniform film having a coating weight between 1 and 4 grams per square meter (g/m^2). The coated plate was exposed under UV-light between 10 and 30 mJ/cm^2 to partially polymerize the coated film. The prime coat shows good adhesion to the aluminum substrate.

[0033] The composition of the IR absorbing layer follows. The solution for coating of the IR absorbing layer was prepared by uniformly mixing the following ingredients:

Ingredients	Suppliers	Weight(%)
Limonene Dioxide	Atochem	20 - 30
1,3-Butadiene homopolymer internally epoxidized	Atochem	20 - 30
Cyracure UVR 6110	Union Carbide	20 - 30
Carbon Black 250	Degussa	15 - 30
Sartomer CD 1010	Sartomer	1 - 10
Byk-361	Bykchemie	0 - 2

[0034] The solution was coated onto the prime coat using a wire-wound rod to give a uniform film having a coating weight between 1 and 2 g/m^2. The plate was exposed under UV-light between 20 and 80 mJ/cm^2 to partially polymerize the coated film. The IR-absorbing layer exhibited good adhesion to the prime coat formed by exposure to UV-light as a result of crosslinking reactions of the remaining epoxy groups on the surface of the prime coat with the epoxy groups of the IR-absorbing layer.

[0035] The top layer was prepared to comprise the following composition:

Ingredients	Suppliers	Weight (%)
PS-445	United Chemical Tech.	80 - 95
Syl-Off 7367	Dow Corning	1 - 10
PS-072	United Chemical Tech.	1 - 10
Allyl glycidyl ether	Aldrich Chemical	1 - 10
Sartomer CD1010	Sartomer	1 - 5

[0036] PS-445 is a divinyl terminated polysiloxane. Syl-Off 7367 is a mixture of polymethylhydrosiloxane and inhibitor. PS-072 is a platinum-vinylsiloxane complex. The solution was coated onto the IR-absorbing layer using a wire-wound rod to give a uniform film having a coating weight between 1 and 2 g/m^2. The coated plate was exposed to UV-light between 80 and 200 mJ/cm^2 to crosslink the topmost layer. Finally, the coated plate was placed in the oven at 150 °C for two minutes to complete the crosslinking reactions. The topmost layer exhibits good adhesion to the IR-absorbing layer which results from the crosslinking reactions of the remaining epoxy groups on the surface of the IR-absorbing layer with the glycidyl groups of the topmost layer during exposure to the UV light.

[0037] Printing images are written on the above plates by using an infrared laser at 830 nm. Upon exposure to the infrared laser light, the IR-absorbing layer was ablated, weakening the silicone top layer bond only over the ablated image area. The weakened surface coating was then rubbed away by using cotton cloth wetted with either water or

isopropanol to produce a clean image printable by waterless or dry lithographic printing techniques.

[0038] The coatings formed on the lithoplates of the invention can be polymerized using any of a variety of known mechanisms for initiation of polymerization reactions: cationic, anionic or free radical initiation. The initiating species can be released to the polymerization media by direct addition to the media or photochemically or thermally as released by a photoinitiator or heat.

[0039] The following Example 2 presents an illustration of the invention wherein the polymerization is initiated by free radical initiators, applicable to variations of the invention containing two or three coatings, e.g., prime, IR and top coatings or just IR and top coatings.

EXAMPLE 2

[0040] The composition of the prime coat follows:

Ingredients	Suppliers	Weight(%)
Viscoat 310 HP	SEC	20-30
SR 355	Sartomer	20-30
EB 657	Radcure	20-30
Irgacure 369	Ciba	2-5
Quantacure ITX	Octel Chemicals	1-3
EB 360	Radcure	0-2
Diarylide AAA yellow pigment	Sun Chemical	0-20

[0041] Viscoat 310 HP is tripropylene glycol diacrylate, SR 355 is tetramethyl propyl tetracrylate. Irgacure 369 and Quantacure ITX are photoinitiators. EB 360 is acrylated silicone. The solution was coated on the smooth aluminum substrate using a wire-wound rod and exposed under UV-light at 200 mJ/cm^2 to give a uniform film having a coating weight between 1 and 4 g/m^2.

[0042] The composition of the IR absorbing layer follows:

Ingredients	Suppliers	Weight(%)
Viscoat 310 HP	SEC	20-30
SR 355	Sartomer	20-30
Irgacure 369	Ciba	2-5
P115	Radcure	1 -3
EB657	Radcure	20-30
Darocur 1173	Ciba	2 - 5
Carbon Black 250	Degussa	10 - 20

[0043] P115 is an acrylated amine. Darocur 1173 and Irgacure 369 are photoinitiators. The solution was coated onto the prime coat using a wire-wound rod. The solution was then exposed to UV light to produce a uniform film. The topmost layer was then coated onto the IR absorbing layer by using a similar coating solution and procedure provided in Example 1. The plate was ablated at 800 mJ/cm^2 by using an infra-red laser which was then subjected to the post cleaning process to produce a printing image.

Claims

1. A waterless, multilayered lithographic printing plate that is imageable by IR laser ablation and exhibits superior print life, said plate comprising:

   a first solid substrate layer;
   a second infra-red light absorbing polymeric layer containing crosslinked functionality;
   a polysiloxane top layer containing crosslinked functionality, wherein said second layer and top layer contain interlayer crosslinked bonds.

2. The plate of claim 1 further comprising a prime polymeric layer interposed between said first and second layer,

said prime layer containing crosslinking functionality connected to said second layer and pigments or dyes to distinguish image bearing and non-image bearing areas of said ablated plate.

3. The plate of claim 1 or 2 wherein said second layer contains UV-visible and infra-red absorbing pigment.

4. The plate of claim 3 wherein said pigment comprises carbon black or graphite.

5. The plate of any of claims 1 to 4 wherein said first layer comprises aluminum or polyester.

6. The plate of any one of claims 1 to 5 wherein said second layer comprises the polymerization reaction product of a solventless mixture of polymerization initiators and polymerizable liquid monomers, oligomers or polymers.

7. The plate of claim 6 wherein said initiators comprise photo-initiated cationic or free radical polymerization initiators.

8. The plate of claim 7 wherein said free radical initiators are selected from benzoin and benzoin ethers, benzilketals, dialkoxyacetophenone derivatives, hydroxyalkylphenones, hydroxyalkylphenones, aminoalkylphenone derivatives, benzophenones derivatives and 1,2-diketones.

9. The plate of claim 7 wherein said cationic initiators are selected from aryldiazonium salts, diaryliodonium salts, triarylsulfonium salts, triarylselenonium salts, dialkylphenacylsulfonium salts, dialkyl-4-hydroxyphenylsulfonium salts and ferrocenium salts.

10. The plate of claim 6 wherein said reaction product is the product of thermally induced polymerization of said liquid monomers, oligomers or polymers.

11. The plate of claim 6 wherein said monomers, oligomers or polymers contain crosslinkable functional groups including epoxide, hydroxy, carboxy, isocyanate, acrylate, vinyl, amino, silane, halohydrin, sulfonate, formyl and aliphatic and aromatic acid anhydrides.

12. The plate of claim 6 wherein said monomers, oligomers or polymers comprise polyethers containing residual epoxy functionality.

13. The plate of any one of claims 1 to 12 wherein said top layer comprises the polymerization reaction product of a solventless mixture of polymerization initiators and polymerizable liquid siloxanes, siloxane oligomers or siloxane polymers.

14. The plate of claim 13 wherein said initiators comprise UV initiated cationic or free radical polymerization initiators.

15. The plate of claim 13 wherein said reaction product is the product of thermally induced polymerization of said liquid silanes monomers, silane oligomers or silane polymers.

16. The plate of claim 13 wherein said silane polymer comprises divinyl terminated polysiloxane.

17. A solventless process for the production of a printing plate preferably according to claim 1, comprising

coating a solid substrate with an IR absorbing solventless mixture of polymerization initiators and polymerizable liquid monomers, oligomers or polymers having crosslinking functionality;
exposing the coated substrate to UV light or heat to partially polymerize the coating;
coating the partially polymerized coating with a polysiloxane containing crosslinking functionality;
exposing the polysiloxane coating to UV light to partially polymerize the coating; and
thermally treating the plate to complete the polymerization and crosslinking reactions.

18. The process of claim 17 including the further step of first coating the substrate with a solventless mixture of polymerization initiators and polymerizable liquid monomers, oligomers or polymers having crosslinking functionality and containing dyes or pigments.

19. A layered image recording material produced by a solventless process and imageable by IR laser ablation to provide a desired image comprising:

a first infra-red light absorbing polymeric layer containing crosslinked functionality;
a polysiloxane second layer containing crosslinked functionality, wherein said first layer and second layer contain interlayer crosslinked bonds.

Patentansprüche

1. Mehrschichtige Druckplatte zum Trockenflachdruck, die durch IR-Laserabtragung mit Abbildungen versehen werden kann und eine ausgezeichnete Druckstandzeit aufweist, wobei die Platte umfaßt:

   eine erste feste Substratschicht;
   eine zweite Infrarotlicht absorbierende Polymerschicht, die vernetzte Funktionalität enthält;
   eine Deckschicht aus Polysiloxan, die vernetzte Funktionalität enthält, wobei die zweite Schicht und die Deckschicht zwischen ihren Schichten vernetzte Bindungen enthalten.

2. Platte nach Anspruch 1, die außerdem eine zwischen der ersten und der zweiten Schicht angeordnete polymere Grundierungsschicht umfaßt, wobei die Grundierungsschicht vernetzende Funktionalität, die an die zweite Schicht gebunden ist, und Pigmente oder Farbstoffe enthält, um bildtragende und nichtbildtragende Bereiche der abgetragenen Platte zu unterscheiden.

3. Platte nach Anspruch 1 oder 2, wobei die zweite Schicht im UV sichtbares und Infrarotlicht absorbierendes Pigment enthält.

4. Platte nach Anspruch 3, wobei das Pigment Ruß oder Graphit umfaßt.

5. Platte nach einem der Ansprüche 1 bis 4, wobei die erste Schicht Aluminium oder Polyester umfaßt.

6. Platte nach einem der Ansprüche 1 bis 5, wobei die zweite Schicht das Polymerisationsprodukt eines lösungsmittelfreien Gemisches aus Polymerisationsstartern und polymerisierbaren flüssigen Monomeren, Oligomeren oder Polymeren umfaßt.

7. Platte nach Anspruch 6, wobei die Starter mit Licht startbare kationische oder radikalische Polymerisationsstarter umfassen.

8. Platte nach Anspruch 7, wobei die radikalischen Starter aus Benzoin und Benzoinethern, Benzilketalen, Dialkoxyacetophenonderivaten, Hydroxyalkylphenonen, Aminoalkylphenonderivaten, Benzophenonderivaten und 1,2-Diketonen ausgewählt sind.

9. Platte nach Anspruch 7, wobei die kationischen Starter aus Aryldiazoniumsalzen, Diaryljodoniumsalzen, Triarylsulfoniumsalzen, Triarylselenoniumsalzen, Dialkylphenacylsulfoniumsalzen, Dialkyl-4-hydroxyphenylsulfoniumsalzen und Ferroceniumsalzen ausgewählt sind.

10. Platte nach Anspruch 6, wobei das Reaktionsprodukt das Produkt der thermisch induzierten Polymerisation der flüssigen Monomere, Oligomere oder Polymere ist.

11. Platte nach Anspruch 6, wobei die Monomere, Oligomere oder Polymere vernetzbare funktionelle Gruppen enthalten, die Epoxid-, Hydroxy-, Carboxy-, Isocyanat-, Acrylat-, Vinyl-, Amino-, Silan-, Halogenhydrin-, Sulfonat-, Formyl- und aliphatische und aromatische Säureanhydridgruppen einschließen.

12. Platte nach Anspruch 6, wobei die Monomere, Oligomere oder Polymere Polyether umfassen, die restliche Epoxyfunktionalität enthalten.

13. Platte nach einem der Ansprüche 1 bis 12, wobei die Deckschicht das Polymerisationsprodukt eines lösungsmittelfreien Gemisches aus Polymerisationsstartern und polymerisierbaren flüssigen Siloxanen, Siloxanoligomeren oder Siloxanpolymeren umfaßt.

14. Platte nach Anspruch 13, wobei die Starter durch UV-Licht startbare kationische oder radikalische Polymerisationsstarter umfassen.

15. Platte nach Anspruch 13, wobei das Reaktionsprodukt das Produkt der thermisch induzierten Polymerisation der flüssigen Silanmonomere, Silanoligomere oder Silanpolymere ist.

16. Platte nach Anspruch 13, wobei das Silanpolymer ein Polysiloxan mit endständigen Divinylgruppen umfaßt.

17. Lösungsmittelfreies Verfahren zur Herstellung einer Druckplatte, vorzugsweise nach Anspruch 1, umfassend

Beschichten eines festen Substrats mit einem IR-absorbierenden lösungsmittelfreien Gemisch aus Polymerisationsstartern und polymerisierbaren flüssigen Monomeren, Oligomeren oder Polymeren mit vernetzender Funktionalität;
Aussetzen des beschichteten Substrates UV-Licht oder Wärme zum teilweisen Polymerisieren der Beschichtung;
Beschichten der teilweise polymerisierten Beschichtung mit einem vernetzende Funktionalität enthaltenden Polysiloxan;
Aussetzen der Polysiloxanbeschichtung UV-Licht zum teilweisen Polymerisieren der Beschichtung; und thermische Behandlung der Platte zum Vervollständigen der Polymerisations- und Vernetzungsreaktionen.

18. Verfahren nach Anspruch 17, das außerdem den Schritt einer ersten Beschichtung des Substrats mit einem lösungsmittelfreien Gemisch aus Polymerisationsstartern und polymerisierbaren flüssigen Monomeren, Oligomeren oder Polymeren, das vernetzende Funktionalität aufweist und Farbstoffe oder Pigmente enthält, einschließt.

19. Schichtweises Bildaufzeichnungsmaterial, hergestellt durch ein lösungsmittelfreies Verfahren, das zur Bereitstellung eines gewünschten Bildes durch Abtragung mit einem IR-Laser mit Abbildungen versehen werden kann, umfassend:

eine erste Infrarotlicht absorbierende Polymerschicht, die vernetzte Funktionalität enthält;
eine zweite Schicht aus Polysiloxan, die vernetzte Funktionalität enthält, wobei die erste Schicht und die zweite Schicht zwischen ihren Schichten vernetzte Bindungen enthalten.

Revendications

1. Plaque lithographique multicouche, à procédé sans emploi d'eau, pour l'enregistrement par ablation des IR au laser, qui manifeste une durée de vie d'impression supérieure, cette plaque comprenant :

une première couche de substrat solide ;
une deuxième couche polymère qui absorbe la lumière infrarouge, porteuse d'une fonction réticulante ;
une couche supérieure de polysiloxane porteuse d'une fonction réticulante, dans laquelle ladite deuxième couche et la couche supérieure possèdent des liaisons intercouches réticulées.

2. Plaque lithographique selon la revendication 1, comprenant, en outre, une couche d'accrochage polymère interposée entre lesdites première et deuxième couches, ladite couche d'accrochage contenant une fonction réticulante liée à ladite deuxième couche et des pigments ou des colorants pour distinguer les parties porteuses d'une image des parties non porteuses d'une image de ladite plaque soumise à ablation.

3. Plaque lithographique selon la revendication 1 ou 2, dans laquelle ladite deuxième couche contient un pigment qui absorbe les ultraviolets dans le spectre visible et les infrarouges.

4. Plaque lithographique selon la revendication 3, dans laquelle ledit pigment comprend du noir de carbone ou du graphite.

5. Plaque lithographique selon l'une quelconque des revendications 1 à 4, dans laquelle ladite première couche comprend l'aluminium ou le polyester.

6. Plaque lithographique selon l'une quelconque des revendications 1 à 5, dans laquelle ladite deuxième couche comprend le produit de la réaction de polymérisation d'un mélange sans solvants d'amorceurs de polymérisation et de monomères, d'oligomères ou de polymères liquides polymérisables.

7. Plaque lithographique selon la revendication 6, dans laquelle lesdits amorceurs comprennent des photoamorceurs de polymérisation de type cationiques ou radicalaires.

8. Plaque lithographique selon la revendication 7, dans laquelle lesdits amorceurs radicalaires sont choisis parmi la benzoïne et les éthers benzoïniques, les benzylcétals, les dérivés de la dialcoxyacétophénone, les hydroxyalkylphénones, les dérivés de l'aminoalkylphénone, les dérivés de benzophénones, et les 1,2-dicétones.

9. Plaque lithographique selon la revendication 7, dans laquelle lesdits amorceurs cationiques sont choisis parmi les sels d'aryldiazonium, les sels de diaryliodonium, les sels de triarylsulfonium, les sels de triarylsélénonium, les sels de dialkylphénacylsulfonium, les sels de dialkyl-4-hydroxyphénylsulfcnium et les sels de ferrocénium.

10. Plaque lithographique selon la revenàication 6, dans laquelle ledit produit de la réaction est le produit de la polymérisation thermoinduite desdits monomères, oligomères ou polymères liquides.

11. Plaque lithographique selon la revendication 6, dans laquelle lesdits monomères, oligomères ou polymères possèdent des groupes fonctionnels réticulables comprenant des fonctions époxyde, hydroxy, carboxy, isocyanate, acrylate, vinyle, amino, silane, halohydrine, sulfonate, formyle, et anhydride d'acides aliphatiques et aromatiques.

12. Plaque lithographique selon la revendication 6, dans laquelle lesdits monomères, oligomères ou polymères contiennent des polyéthers à fonction époxy résiduelle.

13. Plaque lithographique selon l'une quelconque des revendications 1 à 12, dans laquelle ladite couche supérieure comprend le produit de la réaction de polymérisation d'un mélange sans solvants d'amorceurs de polymérisation et de siloxanes, oligomères siloxane ou polymères siloxane liquides polymérisables.

14. Plaque lithographique selon la revendication 13, dans laquelle lesdits amorceurs comprennent des amorceurs cationiques ou radicalaires de polymérisation induite par irradiation sous UV.

15. Plaque lithographique selon la revendication 13, dans laquelle ledit produit de la réaction est le produit de la polymérisation thermoinduite desdits monomères silane, oligomères silane ou polymères silane liquides.

16. Plaque lithographique selon la revendication 13, dans laquelle ledit polymère silane comprend le polysiloxane à terminaison divinyle.

17. Procédé sans emploi de solvants pour la fabrication d'une plaque d'impression, de préférence selon la revendication 1, comprenant les étapes qui consistent à

revêtir un substrat solide avec un mélange sans solvant, absorbant les IR, d'amorceurs de polymérisation et de monomères, oligomères ou polymères liquides polymérisables porteurs d'une fonction réticulante ;
exposer ledit substrat revêtu à une lumière UV ou à une source de chaleur pour polymériser partiellement le revêtement ;
revêtir le revêtement partiellement polymérisé avec un polysiloxane porteur d'une fonction réticulante ;
exposer ledit revêtement polysiloxane à une lumière UV pour polymériser partiellement le revêtement ; et
soumettre la plaque à un chauffage pour terminer les réactions de polymérisation et de réticulation.

18. Procédé selon la revendication 17, comprenant l'étape supplémentaire qui consiste à d'abord revêtir le substrat avec un mélange sans solvants d'amorceurs de polymérisation et de monomères, oligomères ou polymères liquides polymérisables porteurs d'une fonction réticulante et contenant des colorants ou des pigments.

19. Matériau pour l'enregistrement d'une image, multicouche, préparé par un procédé sans emploi de solvants et apte à l'enregistrement par ablation des IR au laser destiné à former une image souhaitée comprenant :

une première couche polymère qui absorbe la lumière infrarouge, porteuse d'une fonction réticulante ;
une seconde couche polysiloxane porteuse d'une fonction réticulante, dans laquelle lesdites première et seconde couches possèdent des liaison intercouches réticulées.